HEAT-RELEASE KINETICS OF AMMONIUM PERCHLORATE IN PRESENCE OF CATALYSTS AND FUEL*†

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ABSTRACT

The rate of heat release of ammonium perchlorate-fuel or ammonium perchlorate-catalyst or both under adiabatic condition was studied as a function of temperature. In the presence of catalysts, the autocatalytic feature associated with nucleation of pure ammonium perchlorate disappears and the adiabatic reaction kinetics follows Arrhenius-type behavior. Studies made with ammonium perchlorate-fuel show that measurable heat release occurs at temperatures below the phase transition temperature of ammonium perchlorate and that the rate of heat generation per mass of material is greater than that of pure ammonium perchlorate. The rate of exothermic decomposition of pure ammonium perchlorate is unaffected by an increase in pressure. This observation suggests that the heat release is controlled by homogeneous or heterogeneous reactions in the condense phase.

Introduction

Measurements of the decomposition kinetics of ammonium perchlorate (AP) were described in a previous publication.[1] In the measurement studies, the rate of heat release under adiabatic conditions was determined as a function of temperature and related to the rate of reaction and nucleation. These determinations have now been extended to AP samples containing catalysts and fuel. Several measurements have also been carried out of the kinetics of exothermic decomposition of AP at elevated pressures to explore the effect of total gas pressure on the reaction.

Experimental Details

As described in detail in Reference 1, the apparatus used in the adiabatic experiments employs a sample in the form of a pressed wafer (30mm in diameter, 4mm in thickness) prepared by pressing about 5 gram of AP-additive mixture at $\sim$ 25000 psi. By this procedure, a hard, durable wafer was produced with a porosity of about 4 to 5 percent in the case of pure AP. The samples containing added fuel were prepared by cutting out a desired dimension of casted AP-carboxy-terminated polybutadiene (AP-CTPB) propellant. A small radial hole near the center of the sample was drilled in each wafer to accommodate a glass sheathed chromel-alumel thermocouple (3 mil wire). The wafer was then clamped between two electrically heated plates that were held in position by spring-loaded bolts.[1] During the course of an experiment, the temperature of the heating plates was continually adjusted to match within less than $0.1^{\circ}C$ that of the interior of the sample, i.e., adiabatic conditions. The sample thermocouple emf was recorded on a strip-chart recorder, while the emf difference between the block and sample thermocouples was displayed

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on the indicating meter of a microvolt amplifier and kept within the
prescribed limits by manual control of the electric power fed to the
heating plates.

In a typical experiment, the block assembly, composed of heating
plates and sample, was placed in a small furnace held at a temperature
of about $250^\circ C$. The sample was brought to a temperature slightly above
$240^\circ C$ by supplying electrical power to the heater plates. The power was
then reduced to establish within the assembly a constant temperature in
the range 240°-$250^\circ C$. Several minutes were generally required for this
process. As the sample temperature began to rise above that of the
heating plates due to exothermic decomposition, electrical power was
supplied to the heater plates at a rate sufficient to maintain a uniform
temperature throughout the sample. The sample temperature history was
recorded until the experiment was terminated due to an excessive rate
of temperature rise (more than $100^\circ C/min$). For the high pressure studies,
a steel vessel was employed that could be heated and pressurized to 200 psi.

The reagent grade crystalline AP was ball milled and sieved into four
fractions with a particle diameter range: (a) less than 43μ, (b) 43-61μ,
(c) 61-88μ, and (d) 88-124μ. The material of a specified particle size
range was then mixed with the desired amount of powdered additive, fuel,
or catalysts or both in a mortar and pestle, and pressed into a pellet.
The compositions of the mixtures studied are summarized in Table 1. The
composition of the casted AP-CTPB propellant was 75wt% AP/25wt% binder.
The AP particle size spectrum for this sample was bimodal, ranging from
2 to 200μ. The particle size of the additives (Fe_2O_3, Cr_2O_3, and Norit A)
was estimated from microscopic examination.

Experimental Results and Discussions

Examination of the experimental data was based on the theoretical
analysis[1] of adiabatic reaction kinetics involving a first order reaction.
According to this analysis, the rate of temperature rise (dT/dt) can be
related to the effective activation energy E for the process: $dT/dt =
p\ e^{-E/RT}$ where the constant p is given by $p = QNA/\rho c$, and Q represents

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the molar heat of reaction, N the molar density, A the preexponential
coefficient of the Arrhenius rate equation, ρ the mass density, and C the
specific heat at constant pressure. A typical example of the experimental
data for the catalyzed decomposition of AP is shown in Figure 1. The re-
sults for a series of additives are summarized in Table 2.

Reproducible results were obtained with samples containing 2.9wt% CC*
and 4.8wt% CC (Table 2); however, the data obtained were less reproducible
than similar data for pure AP, because of (a) difficulty in establishing
isothermal starting conditions, (b) sample fracture during decomposition,
and (c) nonuniform distribution of catalyst throughout the sample. In
the presence of 4.8wt% Cr_2O_3 in the sample, ignition occurred at about
$280^{\circ}C$ so that the adiabatic studies were restricted to a small tempera-
ture interval.

The addition of carbon caused fragmentation of the samples when the
rates of temperature rise exceeded 30 deg/min. Similar but less repro-
ducible results were obtained on substitution of Cabot carbon for Norit A
carbon. Studies of the decomposition rates of three carbon- and catalyst-
containing mixtures[†] (Norit A) were attempted: AP/C (97$\frac{1}{2}$/2$\frac{1}{2}$), AP/CC/C
(95/2$\frac{1}{2}$/2$\frac{1}{2}$), and AP/Cr_2O_3/C (95/2$\frac{1}{2}$/2$\frac{1}{2}$). No definitive data were obtainable
for these ternary carbon-containing mixtures since ignition occurred near
$260^{\circ}C$, corresponding to a rate of temperature rise of only a few degrees/min.

Hematite (Fe_2O_3), a well known burning rate promoter, was examined
as a catalyst for AP decomposition. The results obtained for a mixture
containing 4.8wt% Fe_2O_3, extend to a rate of temperature of 100 deg/min.
It is apparent that catalytic additives, such as metal oxides, alter the
course of decomposition of NH_4ClO_4 and cause ignition or explosion of
the material. In the presence of sufficient concentration of such addi-
tives, the autocatalytic feature of the decomposition of pure NH_4ClO_4
disappears. In such cases, the rate of decomposition follows Arrhenius-
type behavior even at the lowest temperatures examined.

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* Copper chromite.
† All values in weight percent.

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The experimental heat-release rates from the propellant mixture AP-CTPB bring out the interesting fact that the activation energy for the propellant mixture is nearly the same as that previously obtained for pure AP. We may therefore conclude that the rate-controlling process for decomposition is the same in both cases, but the net amount of heat released per mass of material decomposed is greater because of the presence of added CTPB. Some of the intermediates or products resulting from the decomposition of AP are interacting with the added organic fuel. Apparently, such a reaction with heat generation occurs already at temperatures below the transition temperature of AP ($240^{\circ}C$) as demonstrated by the curve in Figure 2. Since exothermic heat generation by homogeneous or heterogeneous reaction in the condensed phase takes place at significantly lower temperatures than in the case of pure AP, the presence of binder should enhance ignition and combustion of such a propellant.

To determine the influence of total gas pressure on the decomposition of AP, the adiabatic measurements were extended to elevated pressures. As shown in Figure 3, the rate of exothermic decomposition of pure AP is unaffected by a more than tenfold increase in pressure. The absence of a pressure effect suggests that, at least for pure AP, the heat release observed in our experiments is controlled by reactions in the solid phase. Heterogeneous reactions at the gas/solid interface would be expected to be influenced by pressure except in the case of high surface density of adsorbate--i.e., a condition in which the rate of reaction on the surface itself rather than the transport of reactant to the surface is rate-limiting. In the presence of catalysts, a different reaction model may prevail. As a matter of fact, the apparent correlation between burning rate of AP/catalyst propellants and catalytic activity for ammonia oxidation strongly indicates the importance of heterogeneous reactions in ignition and combustion.

The implications of these condensed-phase, exothermic reactions on propellant properties are currently under investigation. A measure of their contribution can be seen from the data in Table 2, in which we have computed the heat flux generated by exothermic chemical reaction at a temperature of $800^{\circ}K$, representative of the surface temperature of an AP propellant during steady-state burning and ignition.

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References

1. Inami, S. H., Rosser, W. A., and Wise, H. Trans. Faraday Soc., 1966, 62, 723

2. Evans, M. W., Beyer, R. B., and McCulley, L. J. Phys. Chem., 1964, 40, 2431

Table 1. Composition of Mixtures Used in Adiabatic Studies

| Ammonium perchlorate[*] | Additive | |
Particle size range (μ)	Type	Percent by wt
43-61; 88-124	copper chromite[†]	2.9; 4.8
88-124	chromic oxide[*]	2.5; 4.8
88-124	cupric oxide[‡]	4.8
43-61; 88-124	ferric oxide[*]	4.8
88-124	carbon (Norit A; Cabot-Sterling VR)	2.5
88-124	carbon/copper chromite	2.5/2.5
88-124	carbon/chromic oxide	2.5/2.5

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[*] From Matheson, Coleman, and Bell (reagent grade).
[†] From Harshaw Chemical Company.
[‡] From J. T. Baker Company.

Table 2. Results of Adiabatic Studies*

| Additive	Wt percent	Particle size range (microns)		$\frac{dT}{dt}$ (deg/sec)	$\dot{q}$** cal/cm³ sec
		Ammonium perchlorate†	Additive		
Copper chromite	2.9	43-61	~ 3.5‡	$10^{13.8}$ exp $(-40,000/RT)$	8.4×10^2
Copper chromite	4.8	88-124	~ 3.5‡	$10^{16.5}$ exp $(-43,000/RT)$	6.6×16^4
Copper chromite	4.8	43-61	~ 3.5‡	$10^{17.7}$ exp $(-46,000/RT)$	1.7×10^5
Chromic oxide	4.8	88-124	< 0.5	$10^{27.3}$ exp $(-68,000/RT)$	6.6×10^8
Carbon (Norit A)	2.5	88-124	< 0.5 to 30§	$10^{19.9}$ exp $(-52,500/RT)$	4.2×10^5
Ferric oxide	4.8	88-124	< 0.5	$10^{12.9}$ exp $(-34,300/RT)$	4.2×10^3
Ferric oxide	4.8	43-61	< 0.5	$10^{13.8}$ exp $(-36,600/RT)$	8.3×10^3

* Average of 4 to 8 experiments.
† Particle size screened by mechanical sieving.
‡ Reference 2.
§ Nonspherical particles.
** Heat generation rate at 800°K. For these calculations a density of 1.6 g/cm³ and a specific heat of 0.4 cal/g deg were employed.

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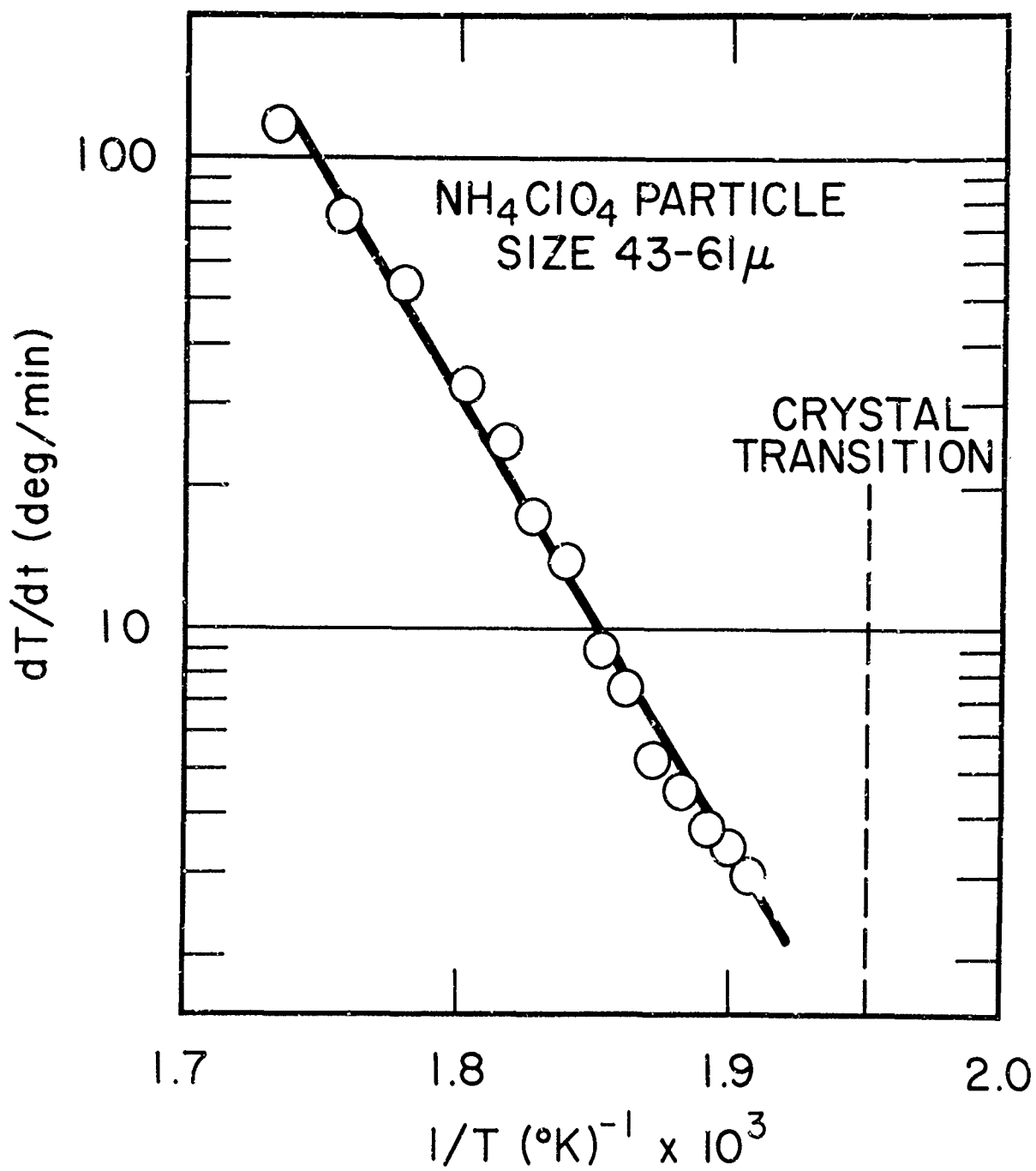
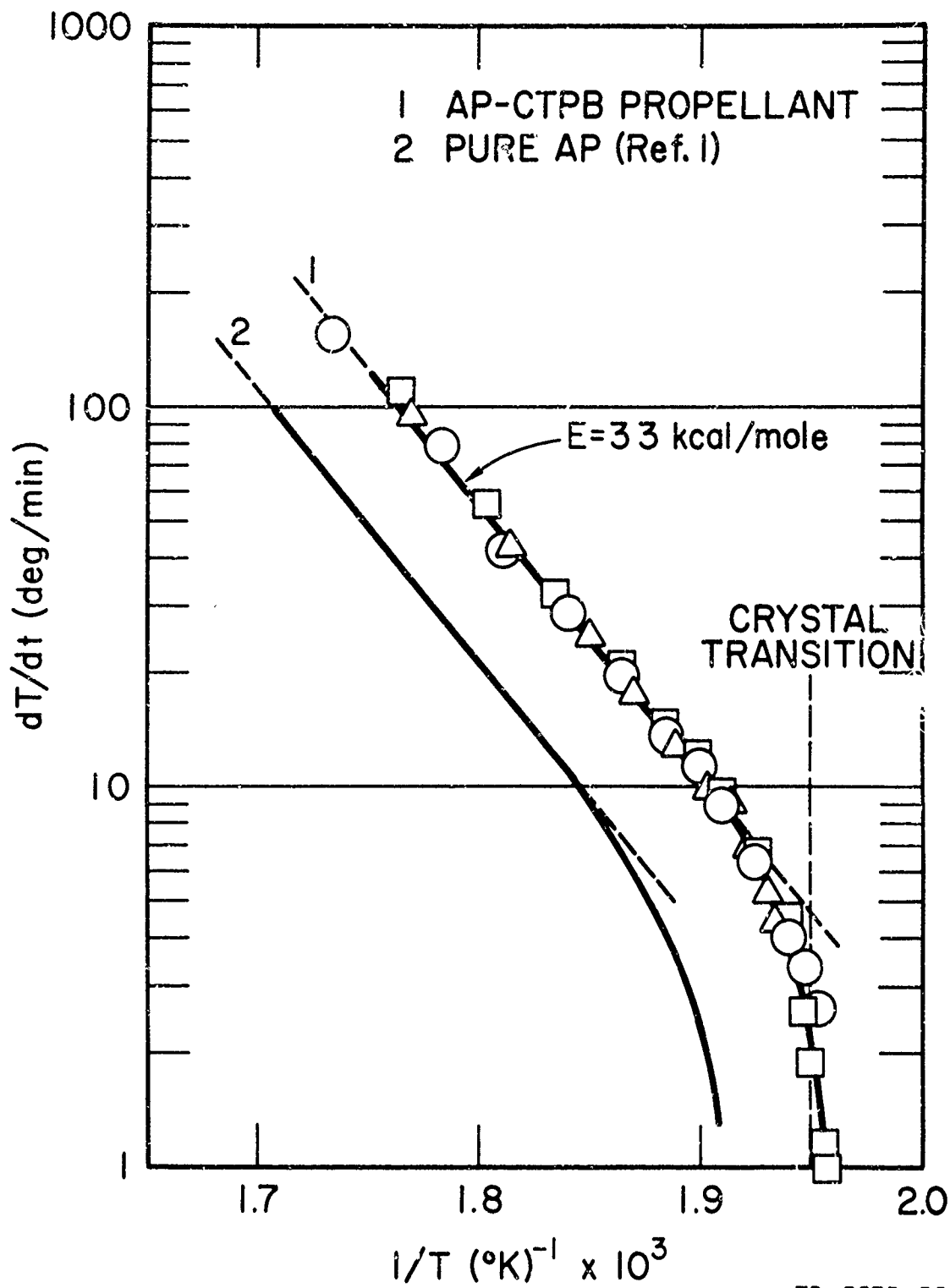FIG. 1 THE ADIABATIC RATE OF DECOMPOSITION OF AN NH$_4$ClO$_4$/4.8wt% CC WAFER

TA-3573-27R
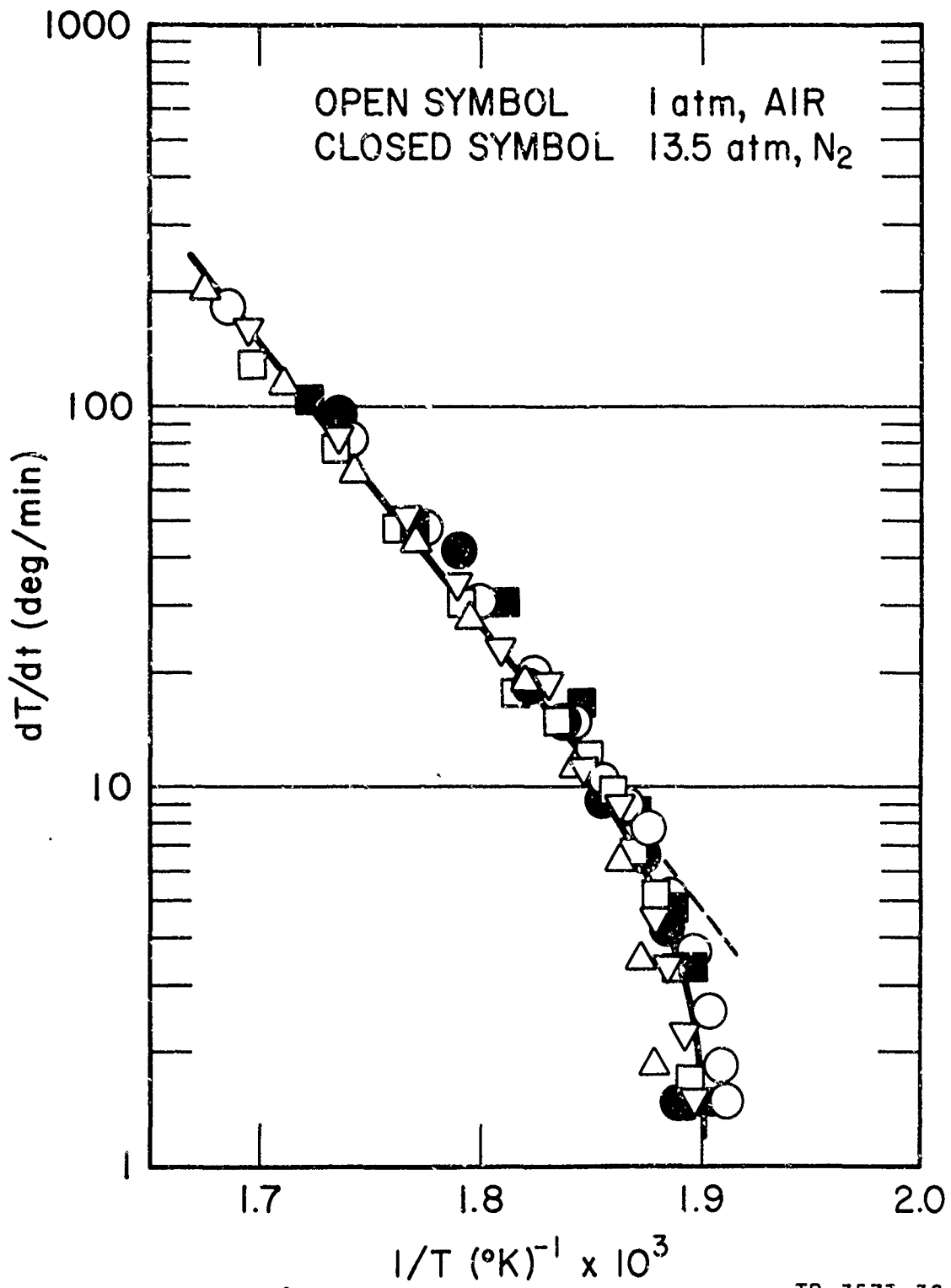
FIG. 2 ADIABATIC DECOMPOSITION RATE OF AP–CTPB PROPELLANT

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FIG. 3 ADIABATIC DECOMPOSITION RATE OF AP AT 1 AND 13.5 ATMOSPHERES
(particle size 61-88μ)

TB-3573-36

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(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
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3. REPORT TITLE

HEAT-RELEASE KINETICS OF AMMONIUM PERCHLORATE IN PRESENCE OF CATALYSTS AND FUEL

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Interim Report

5. AUTHOR(S) *(Last name, first name, initial)*

S. H. Inami, W. A. Rosser, Jr., and H. Wise

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
March 9, 1967	15	2

8a. CONTRACT OR GRANT NO. Nonr-3415(00)	9a. ORIGINATOR'S REPORT NUMBER(S)
b. Authority NR-092-507	PU 3573
c.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	None

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